Electronic Structure of Alkali Carbonates (Li, Na, K and Cs) as Studied by X-Ray Absorption and Emission Spectroscopies

**G. V. Zhuang[a], C. L. Dong[b,c], A. Augustsson[b,d], B. Brena[e],
C. L. Chang[c], Y. Luo[e], J. Nordgren[d], J.-H. Guo[b], and P. N. Ross[a,*]**

[a]Materials Sciences Division and [b]Advanced Light Source Division,
Lawrence Berkeley National Laboratory, Berkeley, CA 94720
[c]Department of Physics, Tamkang University, Tamsui, Taiwan, Republic of China
[d]Department of Physics, Uppsala University, P.O. Box 538, SE-75121, Uppsala, Sweden
[e]Royal Institute of Technology, Theoretical Chemistry, AlbaNova University Center, SE10691,
Stockholm, Sweden

Abstract

We studied the electronic structure of the alkali (lithium, sodium, potassium and cesium) carbonates using soft-x-ray absorption (XAS) and emission (XES) spectroscopies. The unoccupied partial density of states (pDOS) is revealed by C and O *1s* absorption spectra, while the occupied pDOS is reflected by the non-resonantly excited C and O *K*-shell XES spectra. Interpretation of the XES emission spectra was aided by *ab-initio* Hartree-Fock electronic structure calculations. The varying size of the cation produces corresponding changes in the crystal structure (ion packing) as well as the carbon-oxygen bond-lengths within the carbonate anion. We show that the perturbation to the carbonate anion from the larger K and Cs cations lifts degeneracy of the O *1s* core levels, and that these small energy differences are magnified by the interference effect in the resonant inelastic soft x-rays scattering. Subtle differences in the O *2p* DOS as reflected in the O *K*-emission spectra probably represent increasing covalent interaction between the larger K and Cs cations and the oxygen in the carbonate anion.

Key words: alkali carbonates, X-ray absorption, X-ray emission

∗ Corresponding author
 E-mail: pnross@lbl.gov (P.N. Ross).

Introduction

Carbonic acid and its derivatives occupy a special place in the classical theory of valence by Lewis[1] and Pauling[2]. In the classical picture, the C=O double bond in carbonic acid resonates between the three oxygen atoms, the resonance being somewhat inhibited in the acid and its esters, but is complete in the carbonate anion[2]. The resonating structure requires that the carbonate anion has a planar arrangement of atoms with an O-C-O bond angle of 120° and a C-O bond length of 0.131 nm. This configuration was confirmed in the first crystallographic study

of calcite, $CaCO_3$, but later studies revealed that the resonant structure is lost when the anion is placed in a crystal lattice with other cations, specifically the monovalent alkali metal carbonates.[3] The crystal structures of these carbonates clearly indicate a progressive loss of symmetry as the alkali cation increases in size from Li^+ to Cs^+, e.g. from two C-O bond lengths in Li_2CO_3 to three in Cs_2CO_3. Thus, in calcite all the oxygen atoms are equivalent, but in the alkali carbonates they are inequivalent. These changes in oxygen symmetry are a consequence of redistribution of charge within the anion to accommodate the packing of cations of different size and oxygen coordination. In principle, one would expect to see these differences reflected in, for example, the O 1s binding energies of the respective carbonates. But in fact that is not the case.[4] It is likely that sample charging, which can be mitigated but never eliminated from insulator samples, broadens the photoemission spectra such that the differences in binding energy cannot be resolved even with the high resolution available with modern instrumentation. The carbonates thus seem to be an interesting family of compounds to be examined with x-ray absorption (XAS) and X-ray emission (XES) spectroscopies.

Experiment and Computational Methodology

The experiments were performed on beamline 7.0 at the Advanced Light Source, Lawrence Berkeley National Laboratory. The beamline comprises a 99-pole, 5 cm period undulator and a spherical-grating monochromator.[5] XAS spectra were obtained by measuring the fluorescence yield (FY) from the samples, while scanning the incident photon beam energy over the C and O K-edges. The resolution of the monochromator was set to 0.1 and 0.2 eV for the C and O 1s absorption, respectively. The XES measurements were performed using a high-resolution grazing-incidence X-ray fluorescence spectrometer.[6] During the XES measurements the resolution of the florescence spectrometer was set to 0.3 eV and 0.4 eV for the C and O K-emission, respectively, and the resolution of the monochrometer was the same as that of the fluorescence spectrometer. All the alkali (Li, Na, K and Cs) carbonates in powder form were pressed onto indium foil.

For brevity, only the simulated spectra for Li_2CO_3 are presented. A cluster of eleven Li_2CO_3 "molecules" was arranged in such a way that a central Li_2CO_3 "molecule" is surrounded by ten nearby neighbors with all atoms occupying positions of the bulk crystal structure. Simulated x-ray emission spectra were calculated using the generalized group theory formulation of Luo et al..[7] The locally modified DALTON quantum chemistry program[8] was employed for computing the electronic structure and transition moments between molecular orbitals at the Hartree-Fock level. The 6-31G* and 6-31G basis sets are used for the central and surrounding Li_2CO_3 molecules, respectively.

Results and Discussion

The C *1s* absorption spectrum is shown in Figure 1 (upper panel). The most prominent absorption feature originats from the *1s* => π^* transition at 290.2 eV (A$_1$) followed by the multiple-excitation resonance at 297.5 eV (A$_2$) and shape resonance at 303 eV (A$_3$). The C *K*-emission spectra obtained at selected excitation energies at 290.4 eV and 300.9 eV (normal emission) are shown in Figure 1 (lower panel) along with the calculated normal emission spectrum, which is in good agreement with experiment. The *ab-inito* Hartree-Fock (HF) calculation allows the molecular orbital character of the emission features in the XES spectra to be identified. The dominant emission band centered at 279.5 eV (B$_2$) is comprised of several closely spaced C *2p* – O *2p* hybridized valence states. The HOMO is from C *2p* – O *2p* orbital mixture with mainly O *2p* components, which gives rise to a weak feature at 283 eV (B$_3$). There is also a weak contribution from valence states of C *2p* – O *2s* hybridization observed at 265 eV (B$_1$). The weak emission peaks above 285 eV (B$_4$) (i.e. far above the valence band) couldn't be reproduced by the Hartree-Fock (HF) calculation since they are originated from a multiple excitation process. The multiple excitation induced recombination peaks appear only when the excitation energy is above the multiple excitation resonance (297.5 eV) in the C *1s* absorption spectrum.

The O *1s* absorption spectrum of lithium carbonate is shown in Figure 2 (upper panel). The strongest absorption feature located at 533.5 eV (a) is associated with the transition from O *1s* to the C=O anti-bonding orbital (LUMO), while the assignment of the weak features at higher energies is uncertain. The O *K*-emission spectra (curves a and b) presented in Figure 2 (lower panel) show a strong excitation-energy dependence. The emission bands in the normal XES spectrum reflecting the valence states of O *p*-character are well reproduced by the Hartree-Fock calculation. Specifically, the broad feature centered at 526 eV (E$_1$) is mainly from the linear combination of localized O *2p* states, the hybridized C *2p* – O *2p* valence states are centered at 521 eV (E$_2$), and the mixing of O *2p* – C *2s* contributes to a weak emission band at 519 eV (E$_3$). The resonant emission spectrum, when the photon energy is turned to the O *1s* => LUMO resonance (at (a) in upper panel in Fig.2), is also well reproduced by the calculation (see calculated RIXS in the same figure). The RIXS intensity modulation between peaks marked E$_1$′ and E$_1$' is a result of strong interference among three scattering channels in the three degenerate oxygen core levels.

We use the spectral assignments for Li$_2$CO$_3$ to analyse the changes in the electronic structure of the carbonate anion upon increasing ionic radius of cations of (Na, K, Cs). As expected, the C *1s* XES and XAS spectra (not shown) are similar to that for Li$_2$CO$_3$. On the other hand, there is a strong variation in O *K* emission profiles as the alkali metal cation size increases from 0.74 Å of lithium to 1.70 Å of cesium. The strongest variation is observed at the excitation energy of 531.5 eV, i.e. just below the resonant excitation to the LUMO (panel A, Fig.3). The carbonate group in Li$_2$CO$_3$ has nearly 3-fold symmetry around the central

carbon atom, with two CO bond-lengths of 1.286 Å and a third one of 1.271 Å. As the cation size increases, the symmetry is reduced as the cation-anion packing changes to accommodate the larger cation. The RIXS calculations of Li_2CO_3 showed that the interference effect is very sensitive to the local symmetry of the carbonate anion $(CO_3)^{2-}$. Lifting the degeneracy of three oxygen core-holes weakens the interference among the scattering channels and thus the emission profile evolution in Fig. 3 (panel A) is a direct measure of the local symmetry of carbonate anions in the crystal lattice. The observed broadening of the resonance emission profile as the alkali metal cation becomes larger is consistent with the fact that there are three different C-O bond lengths in potassium and cesium carbonates versus two in lithium and sodium carbonates[9]. It would be expected that the variation in ion packing and distortion of the C-O bonding in the carbonate anion with varying cation size would be a consequence of increasing covalency between oxygen and the cation, and that this covalency would be manifest in the O *2p* partial density of states as seen by O *K* emission. In fact, the subtle differences in the O *K* emission (Figure 3, panel B) represent these changes, and further electronic structure calculations of each carbonate will be needed to complete our understanding of the chemical bonding.

Conclusions

We find that the C-O bond in the carbonate anion is highly localized, but cation-oxygen interaction increases with increasing cation size, and as a consequence the crystal structure changes to accommodate larger size cation. The charge redistribution in the anion distorts the C-O bond, and the O *K*-emission exhibits features from this perturbation. In particular, the perturbation from the larger K and Cs cations lifts degeneracy of the O *1s* core levels and these small energy differences are magnified by the interference effect in RIXS. Subtle differences in O *K*-emission represent increasing covalent interaction between the larger K and Cs cations and the oxygen in the carbonate anion.

Acknowledgement

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Figure Captions

Figure 1. Experimental C *1s* absorption (upper panel) and C *K*-emission spectra of Li_2CO_3 obtained at the selected excitation energies (lower panel).

Figure 2. Experimental O *1s* absorption edge spectrum (upper) and selectively excited O *K*-emission spectra (lower) of Li_2CO_3. Excitation energies for the emission spectra are designated by (a and b) in the absorption spectrum.

Figure 3. X-ray emission spectra of alkali carbonates resonantly excited at energy of 531.5 eV (panel A) and non-resonant XES spectra (panel B).

Intensity (a. u.)

Li₂CO₃
C 1s XAS

A₁

A₂

A₃

Intensity (a. u.)

Li₂CO₃
C K-emission

290.4 eV

B₁

B₂

B₃

B₄

300.9 eV

Calculated XES

Energy (eV)